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Development of a Fluorescence-Based in-situ Barium Sensor

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LONG-TERM GOALS

My long-term goal is to contribute to our understanding of coastal ocean circulation through the application of tracer signals for water mass identification. Of particular interest to me is the distinction of freshwater sources, be they riverine, local precipitation or ice melt and the affects of their transport pathways and chemical contents on the health of coastal ecosystems. I believe that for rapid progress to be made, ocean chemists must overcome the limits of bottle based sampling and lab-based analyses. Only then can tracer information be applied to improve the efficacy of operational climate/ecosystem models.

OBJECTIVES

My laboratory group has shown that its biogeochemical characteristics render barium a useful tracer of riverine inputs on the 10's to 100's of km spatial scales. The ultimate objective of this project is to establish a technique for the in-situ determination of barium in seawaters. An intermediate step toward achieving that goal is the development of a ship-board technique so as to be able to use barium distributions to make near real time sampling decisions in the field.

APPROACH

Our analytical detection strategy is to capitalize upon "designer" chelating agents which are relatively specific to Ba and fluoresce in the UV-Vis wavelength range upon complexation. Fluorescence-based measurements can be expected be robust to sea-going conditions and be both sufficiently sensitive (a few to 100's nM) and accurate ($\leq 3\%$) for in-situ deployment. The specialized chelating agents under examination include those multi-dentate fluorescent analogues to diethylene-triaminepentaacetic acid. The major challenge is to overcome interference from the more abundant cations of seawater Ca, Mg and Sr. This project has become the master's thesis of Xuemei Qiu, who joined our laboratory in the fall of 1998 as the recipient of the COAS Dean's merit-based entry-year scholarship. Xuemei came to us with a master's thesis in fluorescence-based environmental chemistry from China. Once Xuemei has identified a suitable analytical procedure, the means of adapting the method to the proven Zero-Angle Profiling System (ZAPS) in-situ chemical fluorometer developed by COAS colleague Gary Klinkhammer will be researched. We hope to capitalize on reagent delivery technology Klinkhammer developed for the ZAPS in-situ Mn detection capability. This project also benefits from the support of my laboratory technician, Tim Wagner and my laboratory assistant, Adrian Avram.

WORK COMPLETED

In 1998, we signed a formal agreement with the company, Molecular Probes of Eugene, Oregon which manufactures "designer" fluorescent chelates, largely for the health industry. They provided us with samples of a variety of chelating agents to examine and proprietary information regarding their chemical composition in exchange for providing them information from our findings for the seawater medium. Our progress to date has been hampered by the condition of available equipment. In early 1998, a mothballed Perkin Elmer UV/VIS 3840 Lambda Array Spectrophotometer and MPF-66 Fluorescence Spectrometer were installed in our laboratory and brought into working condition over the next several months by Tim Wagner. This involved replacement of several electrical components and power supplies in addition to devising methods to record spectra on modern storage media for subsequent computer processing. In spring of 1999, upon completing her first year course requirements, Xuemei Qiu learned to operate this equipment and began to optimize data processing routines for our project. Unfortunately, repeated lamp and various electronic failures limited her progress. In the meanwhile, I joined efforts with other COAS colleagues in leveraging grant monies to obtain modern versions of this equipment. These efforts were successful and a Cary 300 UV-Vis spectrophotometer (joint proposal to OSU with T. Cowles and M. Abbott of COAS) has been purchased and an ISA-Spex Fluorolog 3-1.2 fluorometer (ONR grant to M. Twardowski) will be purchased shortly. These instruments are expected to be installed in my laboratory by early November in the case of the former and by the first of the year in the case of the latter. I also succeeded to leverage ONR support for this project to obtain NSF funding for Xuemei to undertake her master's thesis in my lab upon completion of her first year with support from the Dean's fellowship. Xuemei spent the summer of 1999 developing an automated on-line chromatographic technique for separating Ba at seawater concentrations from the more abundant cations of seawater. She succeeded to accomplish this via a methanesulphonic acid gradient elution from a CS12 cation column using our seagoing Dionex chromatographic system. Progress in the laboratory has been temporarily halted this fall to allow installation of a ventilating clean hood in my laboratory. This hood installation, which facilitate this and other research projects, will be completed by early November. Xuemei will then resume the laboratory component of her thesis involving systematic experiments to check the affects of temperature, pH, salinity and chemical composition upon fluorescent signals of the chelated Ba.

RESULTS

It is too early in the project to report definitive results from our experiments. We have devised a separation and detection schemes that upon combination should permit on-board (controlled ambient conditions) analysis of Ba in seawater. We expect to test this locally at sea in spring 2000.

IMPACT/APPLICATIONS

We intend to apply the ship-board technique to our ongoing field programs in the Arctic and to a field program in the Gulf of Alaska designed to test the significance of buoyancy driven boundary currents on the successful recruitment of salmon yearlings in the Northeast Pacific.

TRANSITIONS

Not yet applicable.

RELATED PROJECTS

1 –G. Klinkhammer of COAS has demonstrated the viability of sensitive and precise absorption measurements by ZAPS; in addition to dissolved Mn, proteinaceous and humic dissolved carbon concentrations, ZAPS has been shown to allow nitrate determinations at 1 micromolar levels in both fresh and seawater matrices. ZAPS has also been engineered to allow either emission or absorption based determinations over the UV-Vis wavelengths. The flexible ZAPS platform should allow the extension of our strategy for in-situ Ba analysis to other elements whose fluorescent chelates are more specific and so pose less stringent interference issues (i.e. Hg, Cd, Sn). The primary interest in this group of elements is contamination detection and control.

2 –Our laboratory has conducted a time-series of Ba analyses in the Beaufort Sea region that further demonstrates the utility of the tracer approach in deciphering water mass origins. Our results allowed us to identify the Mackenzie River as the principal origin of the large freshwater inventory in the region during the Surface Heat Budget of the Arctic 1997-98 deployment. In collaboration with Canadian colleagues we identified changes in atmospheric circulation beginning in 1989 as favoring increased seaice divergence over the past decade (Macdonald et al, 1999). This work reinforces the need to develop in-situ monitoring capabilities of the type we are presently pursuing.

REFERENCES

Macdonald, R. W., E. C. Carmack, F. A. McLaughlin, K. Kenison Falkner and J. H. Swift (1999) Connections among ice, runoff and atmospheric forcing in the Beaufort Gyre, *Geophysical Research Letters*, 26:14:2223-2226.

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